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Exposure to airborne organic compounds inside passenger vehicles

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SUMMARY
Exposure to airborne organic compounds inside passenger vehicles depends on several variables, including the type of fuels used by the car, age of the vehicle, engine capacity, intrusion of combustion products from other vehicles and the mechanical state of the vehicle. In this paper we report the result of a pilot study of the levels of volatile organic compounds, carbonyl compounds and polycyclic aromatic hydrocarbons in a selection of passenger vehicles that were powered by diesel, unleaded petrol and liquefied petroleum gas. Application of hierarchical multivariate modelling to the data revealed the factors that are important in determining the patterns and levels of the pollutants found in the vehicles. In particular, it was observed that the type of fuel was important in determining the level of PAHs while the age of vehicles influenced the levels of the carbonyl compounds. These results as well as exposure reduction strategies are discussed.

KEYWORDS
Organic compounds, Vehicles interiors, Multivariate data analysis.

INTRODUCTION

The search for new clues on the processes that are important in the absorption, emission and complex reactions of indoor air pollutants continues worldwide. Thus several indoor air quality (IAQ) studies have been undertaken and their outcomes have appeared in journals and books devoted to the presence of pollutants in the indoor environment (e.g. Morawska and Salthammer, 2003, Pluschke, 2004, Salthammer, 1999). However, relative to residential and office buildings few of such studies are focused on the interiors of passenger vehicles (Riediker et al, 2003).

This paper presents the levels of carbonyl compounds, the sixteen US EPA Priority polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs) in the interiors of ten cars. The study is significant because (i) an average commuter spends up to 95 min a day (Klepeis, 1999) while professionals such as taxi, bus and truck drivers spend an appreciable part of the day in a vehicle, (ii) passengers travelling in vehicles are exposed to a variety of airborne pollutants, which may have undesirable effects on the health and comfort of the passengers, (iii) airborne pollutant cause unpleasant odours and "fogging" film on the windscreen of vehicles (Bauhof and Wensing, 1999), and (iv) studies focused on exposure to pollutants in the interior of a vehicle can aid the understanding of the daily exposure of individuals to airborne pollutants.

Multivariate data analysis techniques such as PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluation) and GAIA (Geometrical Analysis for

Interactive Aid), principal component analysis and partial least squares have been applied to IAQ data (e.g. Ayoko et al., 2004). Consequently, to examine the structure of and assess the underlying features in the current data, PROMETHEE and GAIA as well as Partial Least Squares, Principal Component Analysis and Hierarchical Principal Component Analysis, which have not featured prominently in IAQ assessment were applied to the data. PROMETHEE, a non-parametric method, provides ranking information, which can be used to choose an object in preference to all others, while GAIA facilitates pattern recognition. The results obtained in the study are discussed in the light of control measures for poor IAQ in the interiors of vehicles.

METHODS

Description of the cars studied

The ten cars consisted of a selection of passenger vehicles that are powered by unleaded petrol, diesel and liquefied petrol gas, and aged between 2 and 19 years old. None of the cars was used by smokers. Two of the cars had 6 cylinders and engine capacities higher than 3 L while seven cars had 4 cylinders and engine capacities below 3 L.

Characteristics of the cars

Questionnaires were used to collect information about the characteristics of the cars and the usual activities of the passengers. This information included the age of the car, engine size, number of cylinders, the odometer reading at the beginning of sampling, the last time the car was tuned and the type of fuel it uses.

Sampling and chemical analyses

Each car interior was sampled under minimum ventilation condition ie with all doors and windows shut. Sampling protocols and analyses for the carbonyl compounds, PAHs and VOCs were performed by adapting guidelines based on US EPA Method TO-17 (1999), US EPA Method TO-11A (1999) and US EPA Method TO-13 A (1999) respectively. Thus carbonyl compounds were sampled onto LpDNPH cartridges (supplied by Supelco, USA), airborne PAHs were sampled onto sorbent tubes containing XAD-2 (supplied by Supelco, USA) and VOCs were sampled onto stainless steel thermal desorption tubes (Perkin-Elmer) filled with 0.3 g Tenax TA (mesh 60/80, Chrompack). The carbonyl compounds and PAHs were analysed by HPLC while the VOCs were quantified by GC/MS (Hewlett-Packard 6890/5972) after thermal desorption with a Perkin Elmer ATD 400, operated 320°C. The quality assurance/quality control measures recommended in each of the US EPA methods were followed.

Multicriteria ranking

Multicriteria ranking of the air quality in the interiors of the cars was performed with Decision Lab 2000 software, which incorporates the multi-criteria decision-making methods, PROMETHEE and GAIA. PROMETHEE, was used to rank the IAQ in the interiors of the cars on the basis of the concentrations of the pollutants or/and the characteristics of the cars. To identify the variables that influence the ranking, GAIA which displayed PROMETHEE results as PC1 (principal component 1) versus PC2 (principal component 2) biplots was employed. The interpretation of PROMETHEE and GAIA results was undertaken as described previously (Ayoko et al. 2004).

Principal Component Analysis, Partial Least Squares and Hierarchical Principal Component Analysis

Principal Component Analysis (PCA) and Partial Least Squares (PLS) (Ayoko et al, 2007) were performed using the concentration of each of the identified compounds while Hieracrchical Principal Component Analysis (HPCA) was performed on the peak areas of the different peaks. For the lattter analysis, each of the chromatograms was divided into 6 blocks and the areas of 10 of the most prominent peaks in each block were recorded as functions of the retention times. Principal Component Analysis was performed for the data for each block and the scores for the first 3 components was obtained for each car. By combining the two results, 6 x 3 = 18 new variables were obtained. These were subsequently subjected to hierarchical principal component analysis using SIMCA P 10 software and Decision Lab 2000.

RESULTS

Survey of the pollutants

Thirteen carbonyl compounds, sixteen polycyclic aromatic hydrocarbons and twenty volatile organic compounds were identified and quantified from the samples. Many compounds listed in the European Collaborative Action (ECA) on Indoor Air Quality (ECA 1997a and 1997b) method for the determination of Total Volatile Organic Compound (TVOC) in indoor environments were not detected in these microenvironments.

Table 1. Summary the concentrations ($\mu g/m^3$) of the most frequently encountered compounds.

Compound	Mean	Median	Max	SD
Formaldehyde	1.3	2.4	13.5	6.7
Acetaldehyde	2.2	3.3	9.7	4.1
Acetone	0.7	1.7	11.2	5.8
Propionaldehyde	0.6	0.9	4.7	2.3
Crotonaldehyde	0.2	0.3	7.0	3.9
Butryaldehyde	0.5	0.4	2.9	1.4
Benzaldehyde	0.1	0.2	8.4	4.8
Valeraldehyde	0.1	0.3	8.2	4.6
Hexaldehyde	0.2	0.8	5.9	3.1
Hexane	91.0	6.0	182.0	88.0
Toluene	224.0	21.0	399.0	189.2
Ethylbenzene	45.0	8.0	56.0	25.1
m-xylene	108.5	14.0	213.0	99.5
Styrene	44.0	6.0	82.0	38.0
α-pinene	2.0	4.0	121.0	68.1
Nonanal	4.5	0.1	15.0	7.7
Fluorene*	3.2	0.1	5.1	2.5
Phenanthracene*	0.5	0.5	1.3	0.4
Anthracene*	1.7	1.8	5.1	2.0
Pyrene	1.7	1.4	4.2	1.5
Benzo (a) anthracene*	1.4	0.3	2.8	1.2
Heptane	0.2	0.0	0.7	0.3
Chrysene*	0.6	0.1	4.0	2.1
Benzo (a) pryrene*	6.6	0.0	10.3	5.2

* Concentrations in ng/m^3

As shown in the Table 1, the highest concentrations for the organic compounds were obtained for traffic generated VOC such as toluene, m-xylene, hexane, styrene and ethylbenzene. However, the concentrations of individual VOCs were generally below the NHMRC target value of less than 250 μg/m^3 for any particular VOC. From the point of view of human health effects it is significant that the level of styrene, which is a well-known carcinogen, is relatively high in the interiors of these cars.

Multivariate data analysis

The cars were ranked on the basis of the concentrations of the VOCs, PAHs and carbonyl compounds found inside them and the result is presented in Figure 1. This showed that vehicle number 5 (V5) had the cleanest air quality on the basis of the analysed compounds while vehicle number 7 (V7) had the worst air quality. GAIA analysis revealed the influence of the compounds on the ranking outcome and it was identified that the most important compounds are: hexane, valeraldehyde, benzo (a) anthracene, fluorene, n-butanol, m-xylene, toluene, benzene, benzaldehyde, hexaldehyde and propionaldehyde. Such ranking information can be used to prioritise remedial action.

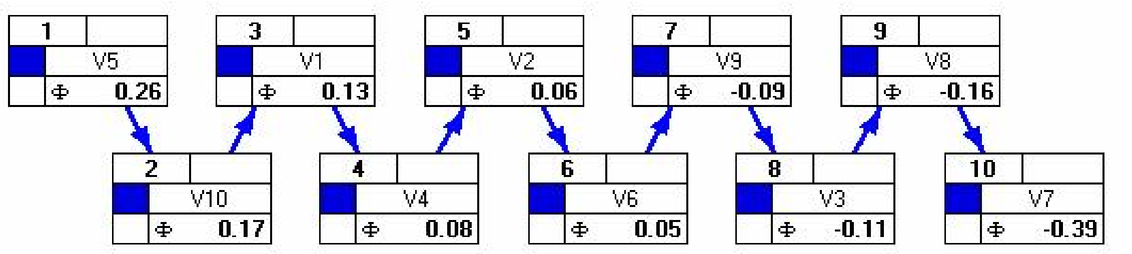

Figure 1. PROMETHEE II ranking for the cars based on their interior air quality. (The cars with the best air qualities are at the extreme left while those with the worst are at the extreme right of the figure.)

To assess the influence of the characteristics of the cars on their interior air quality, a partial least square modelling was conducted. For this analysis, the pollutants were assigned the Y-block and the characteristics of the cars the X-block. The results showed that the fraction of Y that can be predicted Q^2, was greater 0.50 for many of the compounds suggesting that the compounds can be modelled and predicted with car characteristics such as the age of the car, engine size, number of cylinders, the odometer reading at the beginning of sampling, the last time the car was tuned and the type of fuel it uses. To collaborate this, the plot of u1 vs t1 (Figure 2) had a slope of 0.9808, again indicating that the X-block can be used to predict the Y-block l.

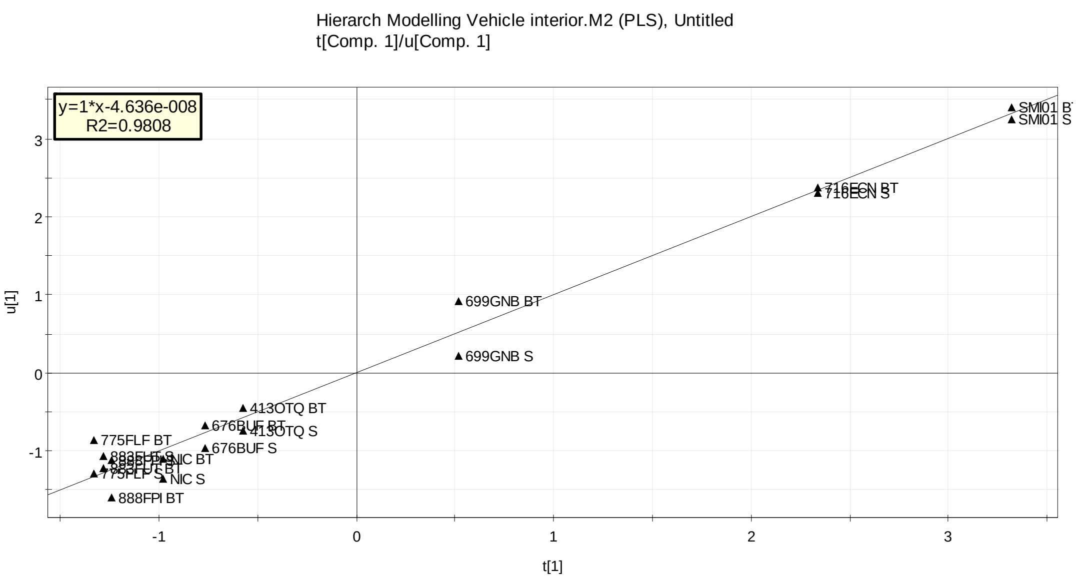

Figure 2. Plot of the PLS first latent variable u{1} (Y-block) versus the PLS first latent variable t{1} (X-block) for the entire data.

To determine the relative influence of each of the car characteristics on the concentration of the compounds a Variable Importance Plot (VIP) was obtained from the PLS model (Figure 3) and this suggested that the mechanical state of the car exerted the most important influence on the air quality of the cars.

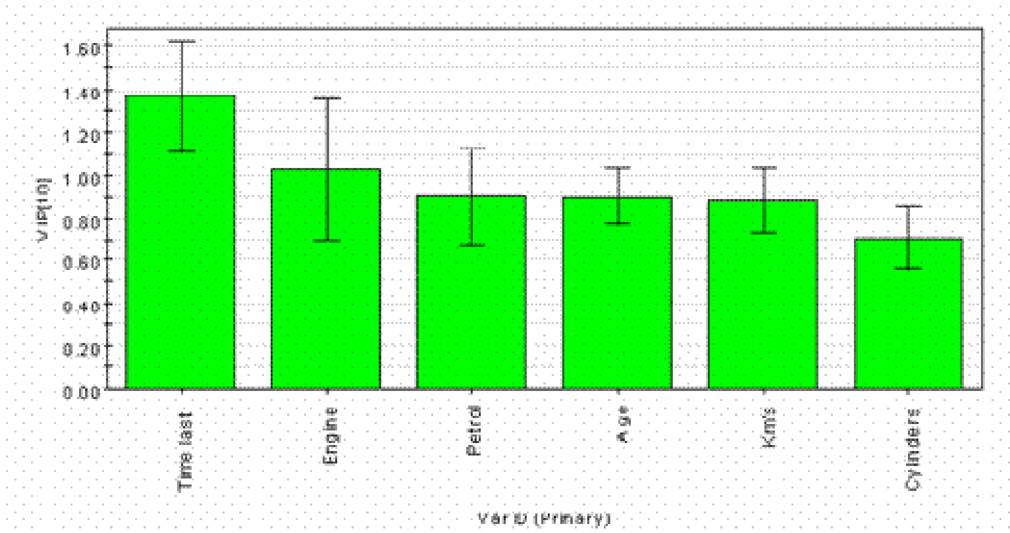

Figure 3. Variable Importance Plot (VIP) obtained from PLS modelling of the relationship between LC retention times and car characteristics (petrol, size of car, age, kilometre covered, time since last service, no of cylinder).

It is instructive to note that while both V5 and V7 (Figure 1) were serviced 1 week before the measurements, V5 is 2 years old car but V7 is 19 years old. This result confirmed that the age of the car also has significant effect on the quality of air in its interior.

However the influence of the type of fuel used by the car and the size of the engine were not apparent from the PCA analysis. Therefore, hierarchical PCA was performed as described in the methods section. The result, presented in Figure 4, indicated that the distribution of the objects on PC1 and PC2 were based on the type of fuel used by each car. ULP cars have negative PC2 scores while LPG and diesel powered cars have positive PC2 scores. In addition, it was possible to distinguish ULP cars with relatively smaller engines from those with comparably larger engines.

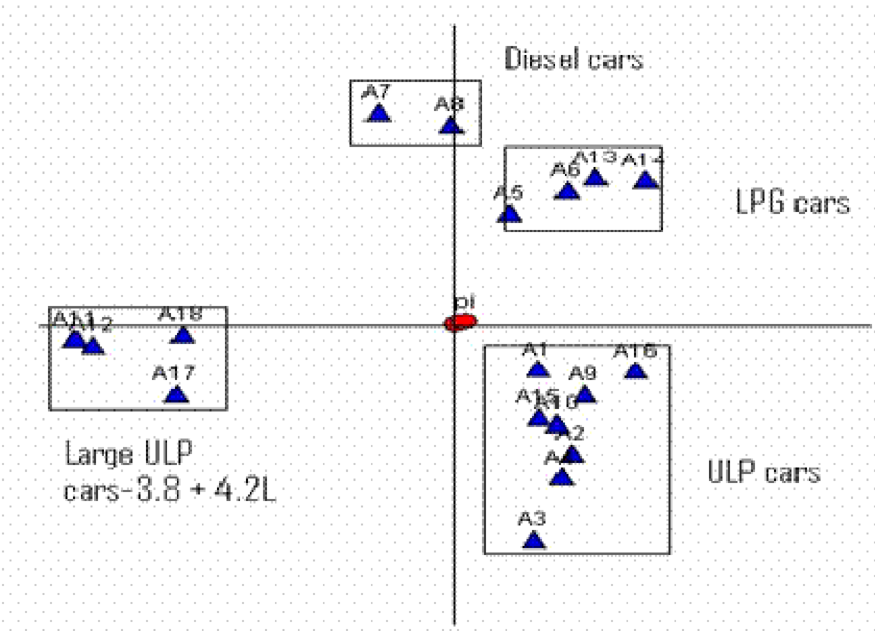

Figure 4. Scores plot for the data obtained from the hierarchical modelling (both PCs explained 72.8% of the data variation).

DISCUSSION

The IAQ of the interiors of passenger cars have been reported and there is evidence that these microenvironments contain compounds that may pose considerable health hazards to passenger. The pollutants may come from the surrounding air, chemicals used in cleaning the cars, abnormal engine operations such as engine oil seal and hydraulic leaks, evaporative loss, and emissions from the cars. Therefore any attempt to reduce exposure to these compounds must take into consideration the various sources of the pollutants and the factors that influence their accumulation in the interiors of cars.

CONCLUSIONS

Through the use of various multi-variate data analysis procedures information that could be used to choose one car interior in preference to another on the basis of their IAQ was made available. Such ranking analysis has not featured prominently in the literature on the indoor quality of car interiors. But they appear to offer a useful tool in prioritizing control strategies. In addition, it was shown that car characteristics such as their ages, mechanical state, engine capacities, type of fuel used are important factors that affect the IAQ of the interior of the cars. Overall, it was evident from the MCDM, PLS and HPCA results that lower levels of pollutants are associated with smaller engines and newer engines, and engines that are well maintained. Because of the small size of the data used, information derived from this study must be used with caution. Nevertheless, they highlight the potential use of multi-variate data analysis procedures in understanding and interpreting IAQ data collected in the interior of passenger vehicles.

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